University Code: 10384
Student ID No.: 20620071154074

厦门大学

MASTER DEGREE THESIS

The Synthesis of the Carboxymethyl Potato Starch with High Degree of Substitution by the Dry Method

By

MUJYAMBERE Jean Marie Vianney

Supervisor: Professor Li Sifang

Program: Chemical Engineering
Date of Graduation: July, 2009

A THESIS SUBMITTED IN FULFILLMENT OF THE REQUIREMENTS FOR THE AWARD OF THE DEGREE OF MASTER OF ENGINEERING

DEPARTMENT OF CHEMICAL AND BIOCHEMICAL ENGINEERING
COLLEGE OF CHEMISTRY AND CHEMICAL ENGINEERING
XIAMEN UNIVERSITY

The Synthesis of the Carboxymethyl Potato Starch with High Degree of Substitution by the Dry Method
Supervisor: Prof. Li Sifang Xiamen University
Name: MUJYAMBERE J.M.V

CERTIFICATION

I, Professor Li Sifang, hereby certify that I have read this manuscript and recommend for acceptance by the Xiamen University a dissertation entitled "The **Synthesis of the Carboxymethyl Potato Starch with High Degree of Substitution by the Dry Method"** in fulfillment of degree of Master of Engineering at Xiamen University, People's Republic of China.

Signed……
Supervisor

Date……

Department of Chemical and Biochemical Engineering
College of Chemistry and Chemical Engineering
Xiamen University
Xiamen, Fujian Province
P.R. China

DECLARATION

The research described in this Master of Engineering thesis was conducted under the supervision of Professor Li Sifang at the Department of Chemical and Biochemical Engineering, Xiamen University. I hereby declare that the work submitted is my own and that appropriate credit has been given where reference has been made to the work of others. I also confirm that it has not been previously or concurrently submitted for any other degree, diploma or any other qualifications at Xiamen University, P.R China or other institutions.

COPYRIGHT

MUJYAMBERE Jean Marie Vianney

Date: 22, June , 2009

ACKNOWLEDGEMENT

I would like to express my gratitude to all those who gave me the possibility to complete this thesis. I'm extremely grateful to the Government of Rwanda for its great support from undergraduate level up to the completion of this work. I also wish to extend my thanks to the Government of People's Republic of China for giving me the scholarship during my studies in China and for its good hospitality.

I'm honored to express my deepest gratitude to my dedicated supervisor Prof. LI Sifang for his guidance during my research, his stimulating suggestions and encouragement helped me in all the time of research. My Chinese lab mates made it a convivial place to work. I want to thank them for all their valuable help and support; they were always accessible and willing to help me. Finally, I wish to express my love and gratitude to all my family and friends. I am indebted to my parents, for their care and love.

ABSTRACT

Starches can be modified in several ways to change their function as additives in products. Starches can have hydrogen replaced by something else, such as a carboxymethyl group, making carboxymethyl starch. They can be cross-linked, where the chains get stuck together into a mesh. Longer carbon chains can also be added, such as carboxyethyl groups, or carboxypropyl groups. Adding bulky functional groups like carboxymethyl and carboxyethyl groups reduces the tendency of the starch to recrystallize and makes it less prone to damage by heat and bacteria. Carboxymethyl groups make the starch more hydrophilic (water loving), and aid in cross-linking. Cross-linking occurs when a hydroxyl group (OH) on one chain bonds with a hydroxyl group on an adjacent chain. This toughens the starch, and helps it resist heat and acids. Carboxymethyl starch is used in food industries as emulsifier, stabilizer and thickener agent to improve texture of food properties. It is also used for nonfood applications, e.g., as paper additive, thickening agent, and auxiliary agent in pharmaceutics.

The present work was undertaken to prepare the Carboxymethyl potato starch (CMS) and cross linked carboxymethyl potato starch (XLCMS) under dry reaction conditions. The influences of the reaction temperature, reaction time, the molar ratio of sodium hydroxide and sodium monochloroacetate (SMCA) to the starch on the degree of substitution (DS) and the reaction efficiency (RE) of CMS have been investigated. CMS prepared under dry conditions showed that the highest DS and RE found was 0.78 and 0.39 respectively. The cross-linked carboxymethyl potato starch with the DS of 0.38 was also synthesized using sodium hexametaphosphate (SHMP) and dichloroacetic acid (DCA) as cross linking agents. Using the rotational viscometer, the highest viscosity of CMS and XLCM found was 1380 mPa.s and 3033mPa.s respectively. Both, CMS and XLCMS were characterized by Fourier transform infrared spectrophotometer and scanning electron microscopy (SEM).

Keywords: Carboxymethyl potato starch, cross linked carboxymethyl potato starch, degree of substitution.

摘要

淀粉能够通过不同的方法改性改变其官能团来作为产品添加剂。能够通过其它官能团来替代其上的氢，比如用羧甲基取代得到羧甲基淀粉。还能够将链键合形成网状结构而交联。羧乙基、羧丙基等这些长碳链也同样能够被引入。通过引入如羧甲基、羧乙基这些具有较大位阻的官能团能够减小淀粉再结晶的倾向从而使其不易受热和细菌的影响而变质。羧甲基使得淀粉更具亲水性，并且能够促进交联。当分子链上的羟基（OH）和相邻链上的羟基键合在一起的时候即发生交联反应。交联反应的发生使得淀粉韧性更强，并能增加其耐热和耐酸性。羧甲基淀粉经常作为乳化剂、稳定剂和增稠剂而运用于食品工业中以此来改善食品品质。它同样还用于非食品中，如纸的添加剂，和制药中的增稠剂、助剂。

本文在干反应条件下制备得到羧甲基马铃薯淀粉（CMS）和交联羧甲基马铃薯淀粉（XLCMS）。考察了反应温度、时间、氢氧化钠和氯乙酸钠（SMCA）的摩尔比、对淀粉改性过程中所合成的 CMS 的取代度(DS)和反应效率(RE)的影响。干法制备条件下得到的最高取代度和反应效率分别为 0.78 和 0.39.同时本研究还以六偏磷酸钠（SHMP）和一氯乙酸（DCA）为交联剂制备得到取代度为 0.38 的交联羧甲基马铃薯淀粉。CMS 和 XLCMS 的粘度用旋转粘度计测定其最高粘度分别为 1380 mPa.s 和 3033 mPa.s。同时还用傅立叶变换红外光谱和扫描电镜对其进行表征。

关键词：羧甲基马铃薯淀粉；交联羧甲基马铃薯淀粉；取代度。

ABBREVIATONS

AGU: Anhydroglucose unit

CMS: Carboxymethyl potato starch.

XLCMS: Cross linked carboxmethyl potato starch.

SMCA: Sodium monochloroacetate.

DS: Degree of substitution.

DS_t: Theoretical degree of substitution.

RE: Reaction efficiency.

SEM: Scanning electron microscopy.

DCA: Dichloroacetic acid.

SHMP: Sodium hexametaphosphate.

CLA: Cross linking agent.

FT-IR:Fourier transform infrared spectrophotometer.

TABLE OF CONTENTS

LIST OF FIGURES

Chapter1. INTRODUCTION

1.1. Starch sources

Starch is the major carbohydrate reserve in plant tubers and seed endosperm where it is found as granules [1], each typically containing several million amylopectin molecules accompanied by a much larger number of smaller amylose molecules. By far the largest source of starch is corn (maize) with other commonly used sources being wheat, potato, tapioca and rice. The estimated world production of starch amounts is 58 million tones, extracted from maize (4.6million), potatoes (3.5million) and the remainder coming from rice and cassava roots (tapioca) [2].

Starch in plants, acts as a reserve food supply for periods of growth, dormancy and germination [3,5].Being a biodegradable polymer with well-defined chemical properties, it has a huge potential as a versatile renewable resource for various material applications in food and nonfood areas. The composition and properties of commercial available starches have been studied extensively [3- 9]. Microscopic studies have revealed that starch granules can vary in shape, size and composition depending on the source of the starch. In general, the appearance of the starch granules varies from small granules (cereals) to large granules (tuber and root), ranging from 1 to 100 μm. The shape of a granule can be oval, spherical, polygonal or truncated.

1.2. Molecular structure of the starch

Starch consists of two types of molecules, amylose (normally 20-30%) and amylopectin (normally 70-80%). Both consist of polymers of α-D-glucose units in the $^4C_1$ conformation. In amylose these are linked - (1→4)-, with the ring oxygen atoms all on the same side, whereas in amylopectin about one residue in every twenty or so is also linked - (1→6) - forming branch-points. The relative proportions of amylose to amylopectin and - (1→6) - branch-points both depend on the source of the starch, for example, amylomaizes contain over 50% amylose whereas 'waxy' maize has almost none (~3%) [13].

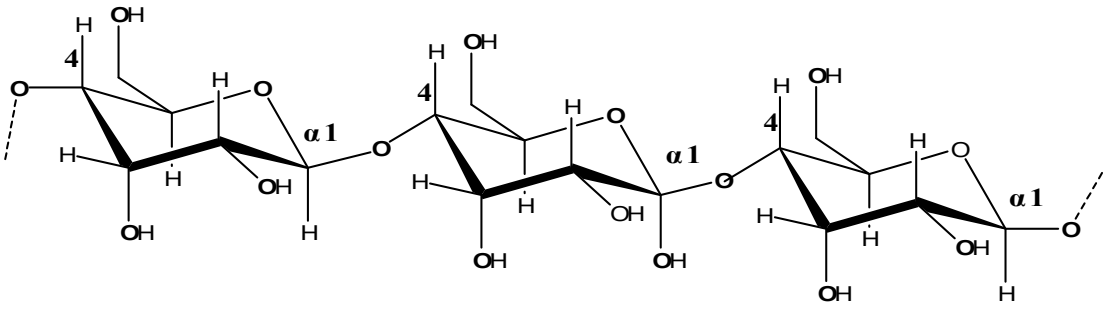

Figure 1.1 Partial structure of the amylose molecule

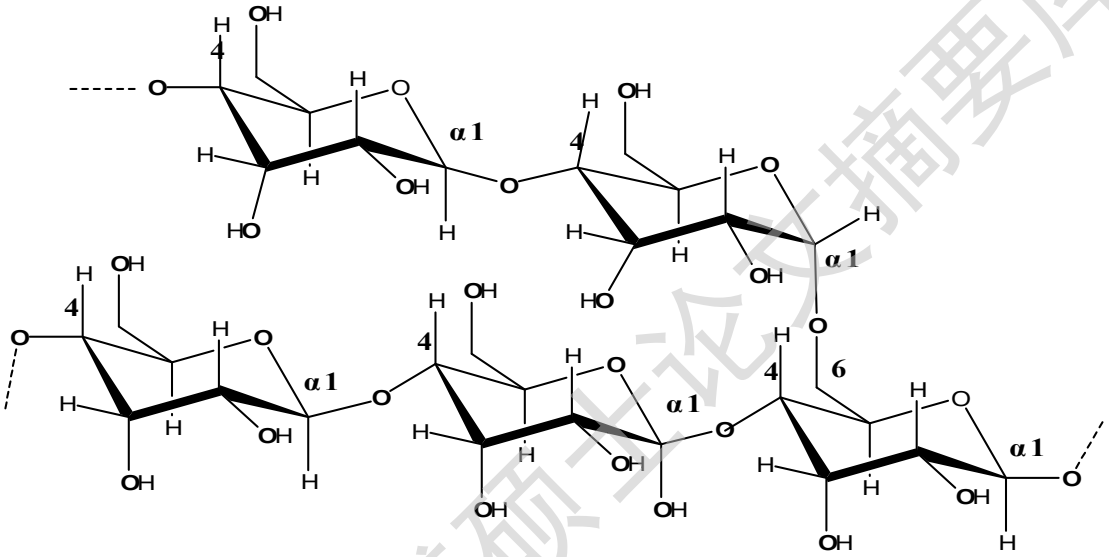

Figure.2 Partial structure of the amylopectin molecule

Amylose and amylopectin are inherently incompatible molecules; amylose having lower molecular weight with a relatively extended shape whereas amylopectin has huge but compact molecules. The presence of amylose tends to reduce the crystallinity of the amylopectin and influence the ease of water penetration into the granules. Most of their structure consists of α-(1⟶4)-D-glucose units. Although the α-(1⟶4) links are capable of relatively free rotation around the (φ) phi and (ψ) psi torsions, hydrogen bonding between the O3' and O2 oxygen atoms of sequential residues tends to encourage a helical conformation. These helical structures are relatively stiff and may present contiguous hydrophobic surfaces.

Amylose

Amylose molecules consist of single mostly-unbranched chains with 500-20,000 α-(1⟶4)-D-glucose units dependent on source (a very few α-1⟶6 branches and linked phosphate groups may be found, but these have little influence on the molecule's behavior [1]). Amylose can form an extended shape (hydrodynamic radius 7-22 nm [11]) but generally tends to wind up into a rather stiff left-handed single helix or form even stiffer parallel left-handed double helical

junction zones [12]. Single helical amylose has hydrogen-bonding O-2 and O-6 atoms on outside surface of the helix with only the ring oxygen pointing inwards. Hydrogen bonding between aligned chains causes retro gradation and releases some of the bound water (syneresis). The aligned chains may then form double stranded crystallites that are resistant to amylases. These possess extensive inter- and intra-strand hydrogen bonding, resulting in a fairly hydrophobic structure of low solubility. The amylose content of starches is thus the major cause of the resistant starch formation.

Single helix amylose behaves similarly to the cyclodextrins by possessing a relatively hydrophobic inner surface that holds a spiral of water molecules, which are relatively easily lost to be replaced by hydrophobic lipid or aroma molecules. It is also responsible for the characteristic binding of amylose to chains of charged iodine molecules (for example, the polyiodides; chains of I_3^- and I_5^- forming structures such as I_9^{3-} and I_{15}^{3-},note that neutral I_2 molecules may give polyiodides in aqueous solution and there is no interaction with I_2 molecules except under strictly anhydrous conditions) where each turn of the helix holds about two iodine atoms and a blue color is produced due to donor-acceptor interaction between water and the electron deficient polyiodides.

Amylopectin

Amylopectin is formed by non-random α-1⟶6 branching of the amylose-type α-(1⟶4)-D-glucose structure. This branching is determined by branching enzymes that leave each chain with up to 30 glucose residues. Each amylopectin molecule contains a million or so residues, about 5% of which form the branch points. There are usually slightly more 'outer' unbranched chains (called A-chains) than 'inner' branched chains (called B-chains). There is only one chain (called the C-chain) containing the single reducing group. A-chains generally consist of between 13-23 residues [10]. There are two main fractions of long and short internal B-chains with the longer chains (greater than about 23-35 residues) connecting between clusters and the shorter chains similar in length to the terminal A-chains [10]. Each amylopectin molecule contains up to two million glucose residues in a compact structure with hydrodynamic radius 21-75 nm [16]. The molecules are oriented radially in the starch granule and as the radius increases so does the number of branches required to fill up the space, with the consequent formation of concentric regions of alternating amorphous and crystalline structure. In the diagram below: A - shows the essential features of amylopectin. B - Shows the organization of the amorphous and crystalline regions (or domains) of the structure generating the concentric layers that contribute to the “growth rings“that are visible by light microscopy. C - Shows the orientation of the amylopectin

molecules in a cross section of an idealized entire granule. D - Shows the likely double helix structure taken up by neighboring chains and giving rise to the extensive degree of crystallinity in granule. There is some debate over the form of the crystalline structure but it appears most likely that it consists of parallel left-handed helices with six residues per turn. An alternative arrangement of interconnecting clusters has been described for some amylopectins [64].

Some amylopectin (for example, from potato) has phosphate groups attached to some hydroxyl groups, which increase its hydrophilicity and swelling power. Amylopectin double-helical chains can either form the more open hydrated Type B hexagonal crystallites or the denser Type A crystallites, with staggered monoclinic packing, dependent on the plant source of the granules [11]. Type A, with unbroken chain lengths of about 23-29 glucose units is found in most cereals.Type B, with slightly longer unbroken chain lengths of about 30-44 glucose units is found in banana, some tubers such as potato and high amylose cereal starches. There is also a type C structure, which is a combination of types A and B and found in peas and beans. Starch granule architecture has been recently described [75].

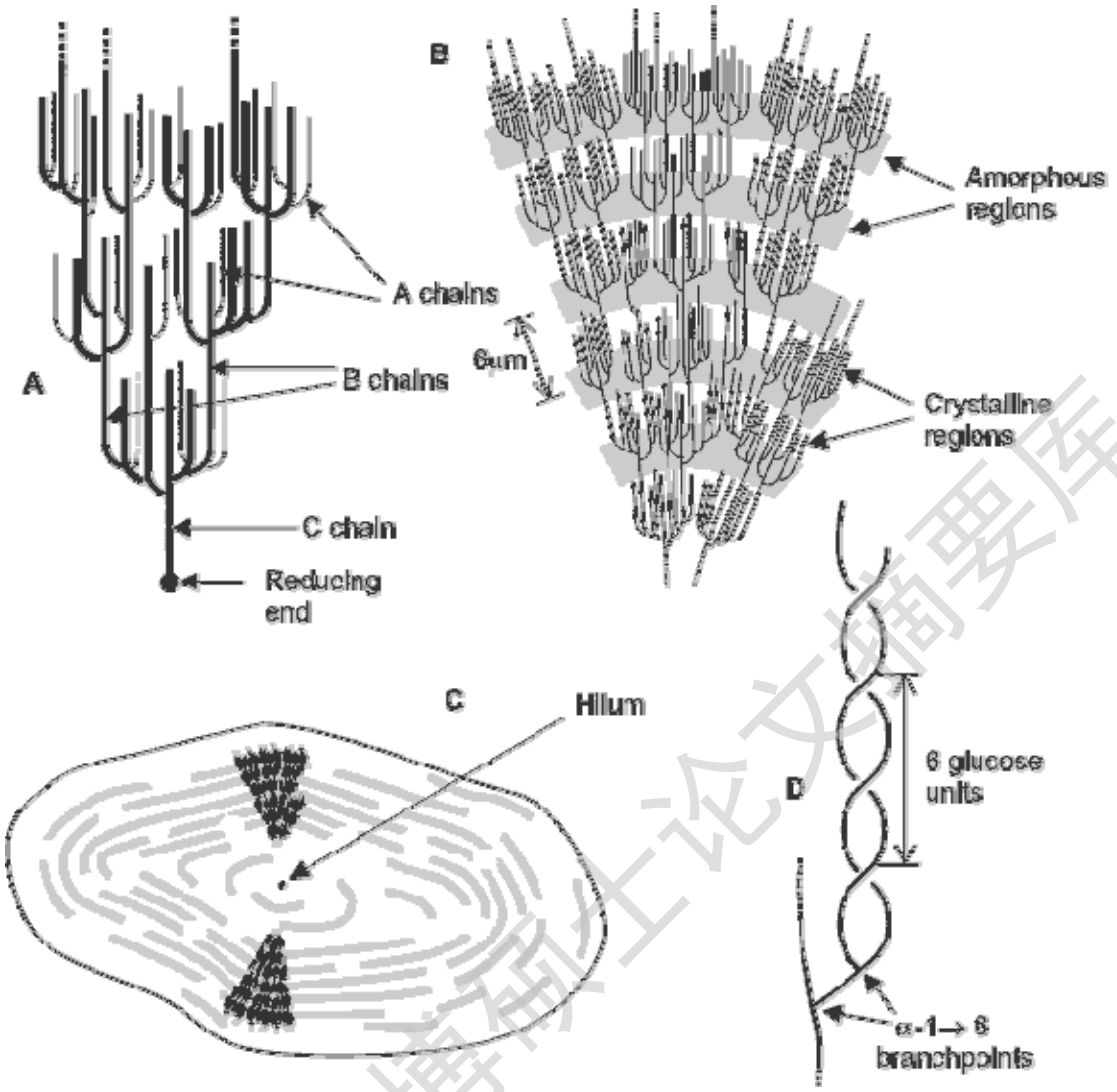

Figure 1.3.The representation of the amylopectin structure (A; B and C chains)

1.3. Chemical modification of the starch

The chemical modification of the starch has been studied as a way to modify its physical-chemical properties, which are limiting the usage of the starch. Modified starch may find application in various non-food industries. Starch based material may be used as substituents for petroleum-based plastic material especially in the packaging industries. Since starches are biodegradable, so they may offer an alternative solution to the disposal problem of petroleum-based materials.

Usually, the starch is modified by chemical reactions and enzymatic treatment. It can also be modified by physical treatment such as extrusion, gelatinization, blending and drying [15, 16, 18]. Chemical modification is based on the reaction of free hydroxyl groups of the AGU monomers with a functional group, resulting in starch derivatives.

The modification involves the esterification or etherification of hydroxyl groups. In general, the modification of the hydroxyl groups in starch in the presence of small amount of base favors O-2 substitution above O-3 and O-6 substitution. The hydroxyl group on C-2 exhibits the highest acidity and therefore the most reactive. However other group may also react because the reactivity of the hydroxyl groups depends on electronic and conformational factors, and their availability on reagents in general [19].

The behavior and properties achieved after chemical modification are depending upon the number, the distribution and the nature of the substituents as well as the starch source and reaction conditions .Those starch derivatives with a degree of substitution up to 0.20 are of commercial importance [5, 18, 19, 20, 21, 22]. Commercially available starch derivatives display a variety of properties which are suitable for industrial applications.

Table 1: Properties and applications of the main commercially available starch derivatives

Modified starch	Reagents	Properties	Applications
1.Acetylated [19,39,40,41]	.Acetic anhydride , .Vinyl acetate	.High viscosity, decreased gelatinization and retrogradation, improved storage stability, good film properties	*Food*: thickeners, stabilizers; *paper*: surface sizing agents; *textile*: warp sizing agents; gummed tapes
2. Phosphorylated [19,42,44,89]	.Phosphoric acid	.Decreased gelatinization, high viscosity, stable dispersion, cohesive texture, polyelectrolyte	*Food*: emulsifiers, thickening agents, adhesives; *paper*: wet-end additives and binders; *textile*: thickeners, warp sizing agents, stiffening; *pharmaceuticals*: detergents;